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In re Application of:
Stamires, Dennis, et al.

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For: DOPED ANIONIC CLAYS



Assistant Commissioner for Patents
Washington, D.C. 20231
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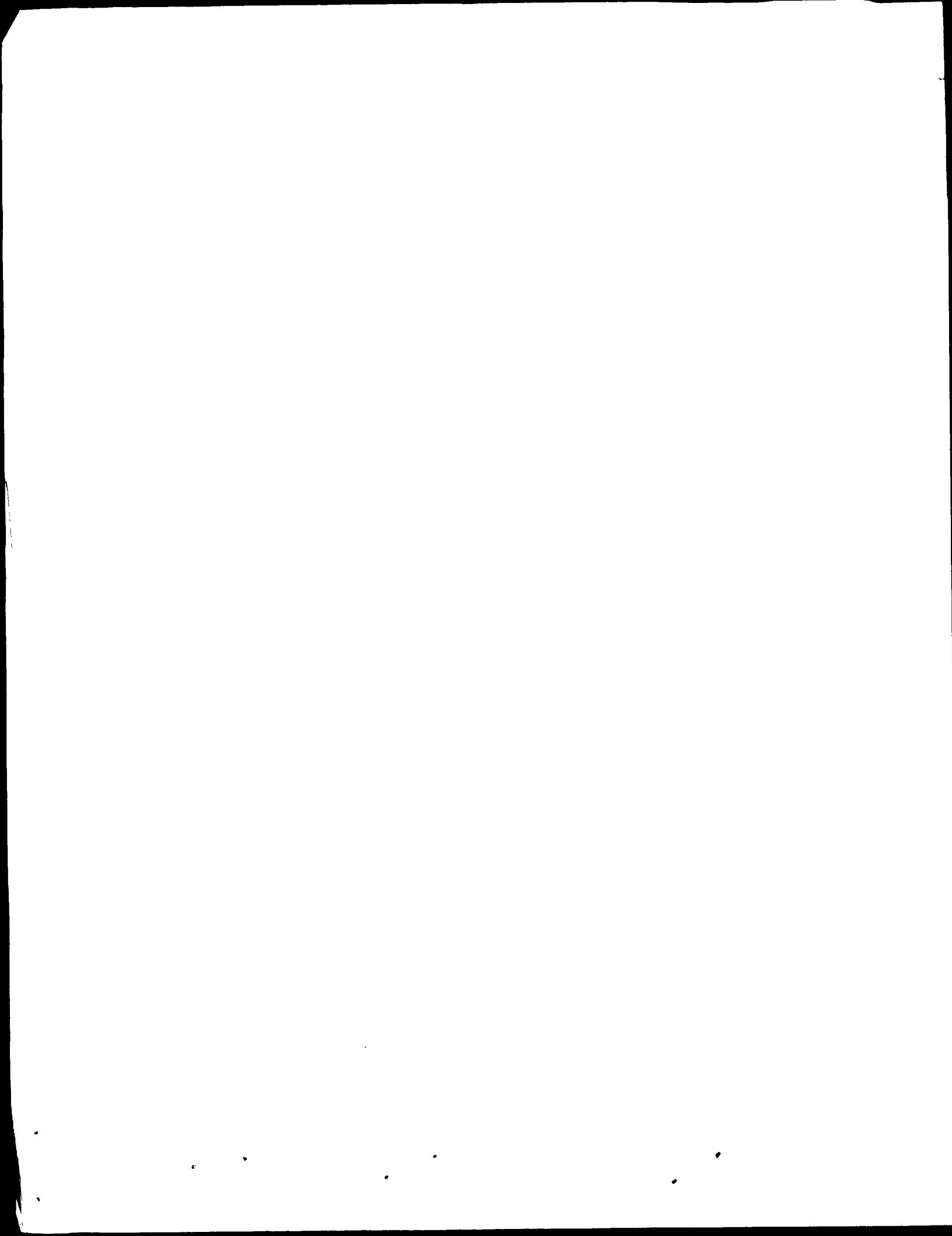
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Sir:

Enclosed herewith is a certified copy of European Patent Application No. 01200831.4, filed March 5, 2001 in connection with the above-identified application.

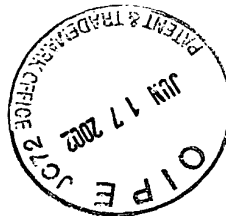
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Attestation

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The attached documents are exact copies of the European patent application described on the following page, as originally filed.
Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°
01200831.4

Der Präsident des Europäischen Patentamts;
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Sheet 2 of the certificate
Page 2 de l'attestation

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Anmelder:
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Doped antonic clays

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Remarques:

1. Confusion, if any, has been cleared up.

1. The first step in the process of identifying a problem is to define the problem. This involves identifying the symptoms of the problem and determining the scope of the problem. Once the problem has been defined, the next step is to identify the causes of the problem. This involves identifying the factors that are contributing to the problem and determining the underlying causes. Once the causes have been identified, the next step is to develop a plan of action. This involves identifying the steps that need to be taken to solve the problem and determining the resources that will be needed to implement the plan. Once a plan of action has been developed, the next step is to implement the plan. This involves carrying out the steps that have been identified in the plan and monitoring the progress of the implementation. Finally, the last step in the process is to evaluate the results of the implementation. This involves determining whether the problem has been solved and whether the resources have been used effectively.

This invention relates to a process for the preparation of doped anionic clays, and doped anionic clays prepared by said process.

5

Anionic clays have a crystal structure which consists of positively charged layers built up of specific combinations of metal hydroxides between which there are anions and water molecules. Hydrotalcite is an example of a naturally occurring anionic clay, in which carbonate is the predominant anion present. Meixnerite is an anionic clay wherein hydroxyl is the predominant anion present.

10

In hydrotalcite-like anionic clays the brucite-like main layers are built up of octahedra alternating with interlayers in which water molecules and anions, more particularly carbonate ions, are distributed. The interlayers may contain anions such as NO_3^- , OH^- , Cl^- , Br^- , I^- , SO_4^{2-} , SiO_3^{2-} , CrO_4^{2-} , BO_3^{2-} , MnO_4^- , HGaO_3^{2-} , HVO_4^{2-} , ClO_4^- , BO_3^{2-} , pillaring anions such as $\text{V}^{10}\text{O}_{28}^{6-}$ and $\text{Mo}_7\text{O}_{24}^{6-}$, monocarboxylates such as acetate, dicarboxylates such as oxalate, alkyl sulphonates such as laurylsulphonate.

20

It should be noted that a variety of terms are used to describe the material that is referred to in this specification as an anionic clay. Hydrotalcite-like and layered double hydroxide is interchangeably used by those skilled in the art. In this specification we refer to these materials as anionic clays, comprising within that term hydrotalcite-like and layered double hydroxide materials.

25

The preparation of anionic clays has been described in many prior art publications. Two major reviews of anionic clay chemistry were published in which the synthesis methods available for anionic clay synthesis have been summarised:

30

F. Cavani et al "Hydrotalcite-type anionic clays: Preparation, Properties and Applications," *Catalysis Today*, 11 (1991) Elsevier Science Publishers B. V.

Amsterdam.

J P Besse and others "Anionic clays: trends in pillary chemistry, its synthesis and microporous solids"(1992), 2, 108, editors: M.I. Occeili, H.E. Robson, Van Nostrand Reinhold, N.Y.

5

In these reviews the authors state that a characteristic of Mg-Al anionic clays is that mild calcination at 500 °C results in the formation of a disordered MgO-like product. Said disordered MgO-like product is distinguishable from spinel (which results upon severe calcination) and from anionic clays. In this specification we refer to said disordered MgO-like materials as Mg-Al solid solutions. Furthermore, these Mg-Al solid solutions contain a well-known memory effect whereby the exposure to water of such calcined materials results in the reformation of the anionic clay structure.

15 Two types of anionic clay preparation are described in these reviews. The most conventional method is co-precipitation (in Besse this method is called the salt-base method) of a soluble divalent metal salt and a soluble trivalent metal salt, optionally followed by hydrothermal treatment or aging to increase the crystallite size. The second method is the salt-oxide method in which a divalent metal oxide is reacted at atmospheric pressure with a soluble trivalent metal salt, followed by aging under atmospheric pressure. This method has only been described for the use of ZnO and CuO in combination with soluble trivalent metal salts.

25 For work on anionic clays, reference is further made to the following articles:

Chemistry Letters (Japan), 843 (1973)
Clays and Clay Minerals, 23, 369 (1975)
Clays and Clay Minerals, 28, 50 (1980)
Clays and Clay Minerals, 34, 507 (1996)
Materials Chemistry and Physics, 14, 569 (1986).

In addition there is an extensive amount of patent literature on the use of

anionic clays and processes for their preparation. Recently, patent applications relating to the production of anionic clays from inexpensive raw materials have been published. These materials include magnesium oxide and aluminium trihydrate.

WO 99/441198 relates to the production of anionic clay from two types of aluminium compounds and a magnesium source. One of the aluminium sources is aluminium trihydrate or a thermally treated form thereof. WO 99/41196 discloses the preparation of anionic clays with acetate as the charge balancing anion from magnesium acetate, another magnesium source and aluminium trihydrate.

15 In WO 99/41195 a continuous process is described for the production of a Mg-Al anionic clay from a Mg source and aluminium trihydrate:

WO 99/41197 discloses the production of an anionic clay-containing composition comprising a Mg-Al anionic clay and unreacted aluminium trihydrate or a thermally treated form thereof.

20 Several patents in the name of Alcoa describe the synthesis of hydrotalcites, i.e. anionic clays, out of magnesium oxide and a transition alumina, in a batch-wise manner and under non-hydrothermal conditions: US 5,728,364 US 5,728,365, US 5,728,366, US 5,730,951, US 5,776,424, US 5,578,286. The comparative Examples 1-3 presented in all these patents indicate that upon using aluminium trihydrate as aluminium source, anionic clays are not formed.

30 There are many applications of anionic clays. These include but are not restricted to: catalysts, adsorbents, drilling muds, catalyst supports and carriers, extenders and applications in the medical field. In particular Van Broekhoven

(US 4,956,581 and US 4,952,382) has described their use in SO_x abatement chemistry.

For several applications the presence of additives, both metals and non-metals, within the anionic clay is desirable. These additives are used to alter or

enhance certain properties of the anionic clay. For instance, Ce and V are added to the anionic clay to obtain material suitable for SO_x removal in FCC. In general, these additives are deposited on the anionic clay by impregnation. With impregnation, however, it is often difficult to obtain a homogeneous dispersion of the additive within the anionic clay or it is difficult to deposit enough additive on the anionic clay to obtain the desired properties.

Some patent publications indicate that the additives may be added to the reaction mixture during preparation of the anionic clay. However, when additives are added to the reaction mixture, their presence may interfere with the anionic clay formation. For instance, when anionic clays are made by co-precipitation it is possible that the pH required to precipitate for example the magnesium and aluminium compounds may not be optimum for precipitation of the additive. In extreme situations the additive may be precipitated in advance of the magnesium and aluminium sources or may not be sufficiently precipitated and remain in solution.

This invention relates to a process for preparing doped anionic clays, wherein the dopant is already incorporated in the starting material. With this process anionic clay can be prepared containing controlled amounts of additive (hereinafter referred to as dopant). Further, the process allows controlled dispersion of the dopant within the anionic clay. The process according to the invention pertains to the preparation of doped anionic clay wherein a trivalent metal source is reacted with a divalent metal source, at least one of the metal sources being either doped boehmite or a doped magnesium source, i.e. doped brucite or doped MgO, to obtain a doped anionic clay.

It was found that when using a doped starting material such as doped boehmite and/or doped magnesium source, the amount of dopant ending up in the anionic clay can be controlled easily, i.e. the dopant can be dispersed homogeneously and enough additive can be deposited on the anionic clay. It was found further that the dopant present either in the magnesium source and/or boehmite does not interfere with the formation of the anionic clay.

Upon being heated anionic clays generally form solid solutions, and at higher temperatures spinels. When used as a catalyst, an adsorbent (for instance a SO_x adsorbent for catalytic cracking reactions), or a catalyst support, the anionic clay according to the invention is usually heated during preparation and is thus in the solid solution form. During use in a FCC unit, the catalyst or adsorbent is converted from an anionic clay into a solid solution.

Therefore, the present invention is also directed to a process wherein a doped anionic clay prepared by the process according to the invention, is heat-treated at a temperature between 300° and 1200°C to form a doped solid solution and/or spinel.

Doped boehmite

As mentioned above, in the process according to the invention a doped boehmite and/or a doped magnesium source is used as starting material for the doped anionic clay. The doped boehmite used in the process according to the invention can be prepared in several ways. In general, a boehmite precursor and an additive are converted to a boehmite containing the additive in a homogeneously dispersed state. Suitable additives are compounds containing elements selected from the group of alkaline earth metals (for instance Ca and Ba), alkaline metals, transition metals (for example Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, W, V, Sn), actinides, rare earth metals such as La, Ce, Nd, noble metals

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such as Pt and Pd, silicon, gallium, boron, titanium, and phosphorus.

5 Suitable compounds containing the desired elements are nitrates, sulphates, chlorides, formates, acetates, oxalates, alkoxides, carbonates, vanadates, etcetera. The use of compounds with heat-decomposable anions is preferred, because the resulting boehmites with additive can be dried directly, without any washing, as anions undesirable for catalytic purposes are not present.

10 Examples of suitable preparation processes for the doped boehmites are described below:

Process 1

15 The boehmite can be prepared by hydrolysing and aging an aluminium alkoxide in the presence of a compound containing the desired additive(s). The additive can be incorporated during the hydrolysis step or added at the end before the aging step.

Process 2

20 The boehmite can be prepared by hydrolysis and precipitation as hydroxides of soluble aluminium salts and aged to form a doped boehmite. Examples of suitable aluminium salts are aluminium sulphate, aluminium nitrate, aluminium chloride, sodium aluminate, and mixtures thereof. The additive(s) may be added while the hydrolysis and precipitation are going on or at the end in the aging step.

Process 3

30 The boehmite can also be prepared by aging an aqueous slurry containing a thermally treated form of aluminium trihydrate and additive(s) at temperatures

5 ranging from 60 to 250°C for a time sufficient to form boehmites, preferably at a temperature between 80 and 150°C. Thermally treated forms of aluminium trihydrate are calcined aluminium trihydrate and flash calcined aluminium trihydrate (CP® alumina). This preparation method has the advantage that no ions are introduced into the boehmite apart from any ions present in the additive compound. That means that with the appropriate choice of additive compounds washing steps can be reduced or avoided altogether. For instance, when decomposable anions (such as carbonates, nitrates, and formates and oxalates) are used, the doped boehmite can be dried directly, as cations undesirable for catalytic purposes are not present.

Process 4

15 The doped boehmite can also be prepared by aging an aqueous slurry containing amorphous alumina gel and additive(s) at temperatures ranging from 60° to 250°C, preferably at a temperature between 80° and 150°C, to form boehmites. Like process 3 mentioned above, this preparation method also has the advantage that no ions are introduced into the boehmite apart from the ions of the additive compound. This means that with the appropriate choice of additive compounds washing steps can be reduced or avoided altogether.

Process 5

25 Doped boehmites to be used according to the invention can also be prepared by aging a relatively amorphous boehmite by thermal or hydrothermal treatment in the presence of compounds of the desired additive to form a boehmite containing additive in a homogeneously dispersed state. More in particular, quasi-crystalline boehmites can be aged in the presence of additive. If this aging is performed under hydrothermal conditions, doped micro-crystalline boehmite will be obtained; if this aging is conducted thermally doped quasi-crystalline boehmite will be obtained.

By using a combination of doped boehmite and non-doped aluminum sources the above-mentioned trivalent metal sources can be used.

30 carbonates, nitrates, chlorides, chlorohydrates, and alkoxides. Also mixtures of manganese sources are the respective oxides, hydroxides, oxalates, cobalt, manganese. Suitable gallium, indium, iron, chromium, vanadium, cobalt, aluminate, as well as sources of gallium, indium, iron, chromium, vanadium, 25 aluminum nitrate, aluminum chloride, aluminum chlorohydrate and sodium flash calcined alumina, gels, non-doped boehmite) aluminum salts such as aqueous suspension such as oxides and hydroxides of aluminum, (e.g. sols, metal sources beside (or other than) doped boehmite may be added to the slurry. As mentioned above, in the process according to our invention trivalent boehmite is added to the reactor in the form of an aqueous suspension or 20 another trivalent metal source can also be used. Preferably the doped combinations of doped boehmites or combinations of doped boehmite and the seed) are introduced into the boehmite.

15 ions other than the ions of the additive (and the optional additives present in described above can suitably be used as a seed. Like processes 3, 4, and 5 no doped with additives. Also boehmites prepared by one of the processes sodium aluminate solutions, etcetera. Additionally, the seeds may have been etcetera), amorphous seeds, milled boehmite seeds, boehmite prepared from 10 commercially available boehmite (Catapal®, Condea P3®, Versal, P-200®, Suitable seeds are the known seeds to make microcrystalline boehmite such as boehmite seeds in the presence of compounds of the desired additives. gibbsite, BOC, and bayerite by hydrothermal treatment, with the aid of suitable Doped Boehmites can also be prepared by aging aluminum trihydrides such as 5

Process 6

No ions other than the ions of the additive compound are introduced into the boehmite with this process.

the amount of dopant present in the final anionic clay can be controlled.

The doped boehmite and other trivalent metal sources may be pre-treated prior to the addition to the reaction mixture. Said pre-treatment may involve treatment with acid or base, thermal and/or hydrothermal treatment, or combinations thereof, all optionally in the presence of seeds. It is not necessary to convert all of the trivalent metal source into doped anionic clay. Excess alumina improves the binding properties of the anionic clay and may also provide different types of desirable functionalities for the anionic clay. For instance, alumina provides acid sites for catalytic cracking and boehmite improves the nickel encapsulation capacity of the anionic clay.

Doped magnesium source

Doped magnesium source, i.e. doped brucite or doped MgO, can be prepared by adding an additive such as the ones described above to brucite, MgO or a precursor thereof in an aqueous suspension and thermally treating said mixture to obtain the doped magnesium source. In this way doped brucite or MgO can be prepared, with the dopants being present in a homogeneously dispersed state.

Suitable brucite or MgO precursors are $Mg(OH)_2$, hydromagnesite, magnesium salts such as magnesium acetate, magnesium formate, magnesium hydroxy acetate, magnesium carbonate, magnesium hydroxy carbonate, magnesium bicarbonate, magnesium nitrate, magnesium chloride, magnesium-containing clays such as dolomite, saponite, sepiolite. Combinations of doped magnesium sources or combinations of a doped magnesium source and another divalent metal source can also be used. Preferably the doped magnesium source is added to the reactor in the form of an aqueous suspension or slurry. As mentioned above, in the process according to our invention divalent metal sources beside (or other than) the doped magnesium source may be added to the aqueous suspension such as metal sources of zinc, nickel, copper, iron, cobalt, manganese, calcium, barium. Suitable zinc, nickel, copper, iron, cobalt,

manganese, calcium, barium sources are oxides, hydroxides, carbonates, nitrates, chlorides. Also mixtures of the above-mentioned divalent metal sources can be used. The divalent metal source may be pre-treated prior to the addition to the reaction mixture. Said pre-treatment may comprise a thermal and/or a hydrothermal treatment, an acid or base treatment, or combinations thereof, optionally in the presence of seeds.

By using of a combination of doped magnesium, source and non-doped magnesium source the amount of dopant in the anionic clay can be controlled.

10 It is not necessary to convert all of the divalent metal source into doped anionic clay. For instance, any excess magnesium, either doped brucite, doped MgO or another magnesium source will usually be present in the final product as brucite, magnesium or alumina-magnesia, doped or not, as the case may be. For the sake of clarity, this excess of magnesium compounds in the anionic clay will be referred to in the description as magnesia. The presence of magnesia or alumina-magnesia in the anionic clay may provide desirable functionalities such as for instance metal trap capacity. The presence of magnesia provides basic sites which render the anionic clay suitable for removing or neutralising strong acid streams of gases or liquids.

20 Doped boehmite and doped magnesium source

25 In the embodiment in which both doped boehmite and doped magnesium source are used in the process, the additive (dopant) in these doped compounds can be same or different.

Conditions

30 The doped starting material(s) and optionally additional divalent and/or trivalent metal sources are added to a reactor and heat-treated in aqueous suspension to obtain a doped anionic clay. Within the context of this invention a reactor is

considered to be any confined zone in which the reaction between the trivalent metal source and divalent source takes place. The reactor may be equipped with stirrers, baffles, etcetera to ensure homogeneous mixing of the reactants. The reaction can take place with or without stirring and at temperatures between 50° and 100°C at atmospheric pressure and at higher temperatures (up to 400 °C) at increased pressure, i.e. under hydrothermal conditions. The reactor may be heated by any heating source such as a furnace, microwave, infrared sources, heating jackets (either electrical or with a heating fluid), lamps, etcetera.

10 Said aqueous suspension in the reactor may be obtained by either adding slurries of the starting materials, either combined or separate, to the reactor or adding the divalent metal source to a slurry of trivalent metal source or vice versa and adding the resulting slurry to the reactor. It is possible to treat, for instance the doped boehmite slurry at elevated temperature and then add either the divalent metal source per se, or add the divalent metal source in a slurry or solution either to the reactor or the doped boehmite slurry.

20 The process according to the invention may be conducted batch-wise or in a continuous mode, optionally in a continuous multi-step operation. The process may also be conducted partly batch-wise and partly continuously.

25 The final anionic clay may conveniently be obtained by drying the resulting mixture.

30 If desired, organic or inorganic acids and bases, for example for control of the pH, may be fed to the reactor or added to either the divalent metal source or the trivalent metal source before they are fed to the reactor. An example of a preferred pH modifier is an ammonium base, because upon drying no deleterious cations remain in the anionic clay.

The product formed may optionally be calcined at temperatures between 300° and 1200°C, preferably between 300° and 800°C and most preferred between 300° and 600°C. This calcination is conducted for 15 minutes to 24 hours, preferably 1-12 hours and most preferred 2-6 hours. By this treatment the anionic clay will be transformed into a solid solution and/or spinel. Solid solutions possess the well known memory effect, which means that they can be transformed back into anionic clays upon rehydration. This rehydration can be performed by contacting the solid solution with water for 1-24 hours at 65°-85°C. Preferably, the slurry is stirred and has a solids content ranging from about 10 to 50 wt%. During this treatment additives can be added.

If desired, the doped anionic clay prepared by the process according to the invention may be subjected to ion-exchange. Upon ion-exchange the interlayer charge-balancing anions are replaced with other anions. Said other anions are the ones commonly present in anionic clays and include pillaring anions such as $V_2O_7^{4-}$, $HV_2O_4^{12-}$, $V_3O_9^{3-}$, $V_{10}O_{28}^{8-}$, $Mo_7O_{24}^{6-}$, $PW_{12}O_{40}^{3-}$, $B(OH)_4^-$, $[B_3O_3(OH)_4]^-$, $[B_3O_3(OH)_5]^{2-}$, $B_4O_5(OH)_4^{2-}$, HBO_3^{2-} , $HGaO_3^{2-}$, CrO_4^{2-} , Keggin-ions, formates, acetate, and mixtures thereof. Examples of suitable pillaring anions are given in US 4,774,212 which is included by reference for this purpose. Said ion-exchange can be conducted before or after drying the anionic clay-containing composition formed in the slurry.

The process of the invention provides wide flexibility in preparing products with a wide range of divalent to trivalent metal ratios. This ratio can vary from 0.1 to 10, preferably from 1 to 6, more preferred from 2 to 4, and especially preferred close to 3.

In addition to the additives already incorporated into the anionic clay by using the doped boehmite or doped magnesium source, it may be desirable to add additional additives, both metal compounds and non-metal compounds, such as rare earth metals, Si, P, B, group VI, group VIII, alkaline earth (for instance

30 bodies. The resulting doped anionic clays may optionally be shaped to form shaped bodies. If composites containing doped anionic clay and (doped) boehmite are formed, this boehmite can serve as a binder and create porosity in the shaped bodies.

25 traction in FCC, SO_x and NO_x removal in FCC, and as a metal trap. appears especially suitable for sulphur removal from the gasoline and diesel matrix for catalysts for hydrocarbon conversion. Moreover, these compositions These compositions appear to be highly suitable for use as an additive or as a metal compound and/or trivalent metal compound.

20 phases such as in physically mixed mixtures of doped anionic clay, divalent trivalent metal compound are intimately mixed, rather than present as separate In said compositions the doped anionic clay, divalent metal compound, and/or the invention by controlling the process conditions:

15 metal compound and a divalent metal compound with the process according to It is even possible to prepare compositions containing anionic clay, trivalent usually in the form of an oxide or hydroxide. composition containing doped anionic clay and a divalent metal compound, On the other hand, divalent metal sources may be used in excess to obtain a form of an oxide or hydroxide.

10 If an excess of trivalent compound is used a composition is obtained which contains doped anionic clay and also trivalent metal compound usually in the form of an oxide or hydroxide.

5 as chlorides, nitrates etcetera. compounds or non-metal compounds are oxides, halides or any other salt such reactor or added to the reactor separately. Suitable sources of metal divalent metal source or the trivalent metal source which are added to the anionic clay according to the invention or they can be added either to the Sn, V, W), to the anionic clay. Said additives can be deposited on the doped Ca and Ba) and/or transition metals (for example Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo,

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The doped anionic clay-containing bodies may also be prepared to contain conventional catalyst components such as matrix or filler materials (e.g. clay such as kaolin, titanium oxide, zirconia, alumina, silica, silica-alumina, bentonite etcetera), molecular sieve material (e.g. zeolite Y USY zeolite, ion-exchanged zeolite, ZSM-5, beta-zeolite, ST-5 etcetera). Typically, such conventional catalyst components or precursors thereof may be added prior to the shaping step.

Suitable shaping methods include spray-drying, pelletising, extrusion (optionally combined with kneading), beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. The amount of liquid present in the slurry used for shaping should be adapted to the specific shaping step to be conducted. It might be advisable to partially remove the liquid used in the slurry and/or add an additional or another liquid, and thus change the pH of the precursor mixture to make the slurry gellable and thus suitable for shaping. Various additives commonly used in the various shaping methods such as extrusion additives may be added to the precursor mixture used for shaping.

20 The doped anionic clay can suitably be used as a component of a catalyst composition.

The present invention is illustrated by the following examples.

EXAMPLES

Example 1

5 A suspension of Condea P-3® alumina in a $Zn(NO_3)_2$ solution was homogenised by high shear mixing for 15 minutes. The mixture was aged at 85°C for 24 hours. This resulted in a Zn^{2+} doped boehmite containing around 10 wt% ZnO .

10 To the doped boehmite-containing slurry a MgO-containing slurry with a pH of 7.42 and a temperature of 44°C was added in an amount sufficient to obtain a Mg/Al molar ratio of 2.3. Subsequently, the mixture was aged at 85°C for 24 hours. The slurry had a solids content of approximately 25 wt% and a pH of 8.92. The final product was dried at 100°C. Powder X-ray diffraction (PXRD) indicated the formation of anionic clay.

Example 2

15 A suspension of Condea P-3® alumina in a $Zn(NO_3)_2$ solution was homogenised by high shear mixing for 15 minutes. The mixture was aged at 85°C for 24 hours. This resulted in a Zn^{2+} doped boehmite containing around 10 wt% ZnO .

20 To the doped boehmite-containing slurry a MgO-containing slurry with a pH of 7.42 and a temperature of 44°C was added in an amount sufficient to obtain a Mg/Al molar ratio of 2.3. Subsequently, the mixture was aged hydrothermally at 165°C and autogenous pressure for 2 hours. The slurry had a solids content of approximately 25 wt% and a pH of 8.92. The final product was dried at 100°C. PXRD indicated the formation of anionic clay.

Example 3

30 A suspension of Condea P-3® alumina in a $Zn(NO_3)_2$ solution was

30 MgO was added to the slurry. The resulting slurry had a pH of 8.92, a solids content of about 25 wt% and a temperature of 52°C. The Mg/Al ratio in the

25 CeO₂-doped boehmite was prepared by suspending Condea P-3® alumina in a (NH₄)₂Ce(NO₃)₆ solution with a pH of 7.42 and a temperature of 44°C with high shear mixing for 15 minutes. The suspension was treated at 85°C for 24 hours. The product was not dried. The resulting doped boehmite containing around 10 wt% CeO₂.

Example 5

20 aged at 80°C for 12 hours. The product was filtered and dried overnight at 100°C. PXRD indicated the formation of anionic clay. MgO and Na₂CO₃ (final concentration 1M) were added to the doped boehmite-containing slurry. The Mg/Al ratio in the slurry was 2.3. The resulting slurry was

15 La₂O₃. subsequently dried at 90°C overnight. The doped boehmite contained 10 wt% the presence of La(NO₃)₃. The precipitate was aged at 80°C for 24 hours and aluminium sulphate and sodium aluminate to a final pH of 10, at 85°C and in

La₂O₃-doped quasi-crystalline boehmite was prepared by co-precipitating

Example 4

10 To the doped boehmite-containing slurry a MgO-containing slurry with a pH of 7.42 and a temperature of 44°C was added in an amount sufficient to obtain a Mg/Al molar ratio of 2.3. Following addition of NaOH/Na₂CO₃ (1M final concentration), the mixture was aged at 85°C for 24 hours. The initial pH of the slurry was 10. The product was filtered, washed with water and dried at 100°C. PXRD indicated the formation of anionic clay.

5 wt% ZnO. homogenised by high shear mixing for 15 minutes. The mixture was aged at 85°C for 24 hours. This resulted in a Zn²⁺ doped boehmite containing around 10

slurry was 2.3. The slurry was aged at 85°C for 24 hours. The product was dried overnight at 100°C. PXRD indicated the formation of anionic clay.

Example 6

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CeO_2 -doped boehmite was prepared by suspending Condea P-30 alumina in a $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ solution with a pH of 7.42 and a temperature of 44°C with high shear mixing for 15 minutes. The suspension was aged at 85°C for 24 hours. The product was not dried. The resulting doped boehmite containing around 10 wt% CeO_2 .

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MgO was added to the slurry. The resulting slurry had a pH of 8.92, a solids content of about 25 wt% and a temperature of 52°C. The Mg/Al ratio in the slurry was 2.3. The slurry was aged hydrothermally at 165°C at autogenous pressure for 4 hours. The product was dried overnight at 100°C. PXRD

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indicated the formation of anionic clay.

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CLAIMS:

(44)

1. Process for the preparation of doped anionic clay wherein a trivalent metal source is reacted with a divalent metal source, at least one of the metal sources being either doped boehmite, doped MgO or doped brucite, to obtain a doped anionic clay.

2. Process according to claim 1, wherein doped boehmite is reacted with a divalent metal source.

3. Process according to claim 1 or 2, wherein doped brucite is reacted with a trivalent metal source.

4. Process according to any one of the claims 1-3, wherein doped MgO is reacted with a trivalent metal source.

5. Process according to claim 2 wherein in addition to the doped boehmite another trivalent metal source is present in the reaction mixture.

6. Process according to claim 3 wherein in addition to the doped brucite another divalent metal source is present in the reaction mixture.

7. Process according to claim 4 wherein in addition to the doped MgO another divalent metal source is present in the reaction mixture.

8. Process according to any one of claims 1-7 wherein the trivalent metal source and the divalent metal source are reacted under hydrothermal conditions.

9. Process according to any one of claims 1-8 wherein the doped boehmite, the doped MgO and/or the doped brucite contain a rare earth metal

- compound.
10. Process according to any one of the previous claims, wherein the doped boehmite, the doped MgO and/or the doped brucite is added in excess to obtain a compositions comprising anionic clay and doped boehmite, doped MgO and/or doped brucite.
11. Process for the preparation of a doped Mg-Al solid solution and/or spinel, wherein an anionic clay obtained by any one of the processes according to any one of the previous claims is subjected to a heat-treatment at a temperature between 300° and 1200°C.
12. Process for the preparation of doped anionic clay, wherein the Mg-Al solid solution obtained by the process of claim 11 is rehydrated to form a doped anionic clay.
13. Doped anionic clay obtainable the process according to any one of claims 1-10 or 12.
14. Shaped body comprising doped anionic clay according to claim 13.
15. Catalyst composition containing doped anionic clay according to claim 13.
16. Catalyst additive composition containing doped anionic clay according to claim 13.

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claim 13.

The present invention is directed to a process for the preparation of a doped anionic clay. In said process a trivalent metal source is reacted with a divalent metal source, at least one of the metal sources being either doped boehmite, doped MgO or doped brucite, to obtain a doped anionic clay.

Suitable dopants are compounds containing elements selected from the group of alkaline earth metals (for instance Ca and Ba), alkaline metals, transition metals (for example Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, W, V, Sn), actinides, rare earth metals such as La, Ce, Nd, noble metals such as Pt and Pd, silicon, gallium, boron, titanium, and phosphorus.

ABSTRACT

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